
Consistent Modifications of SINDO1: II. Applications to First- and Second-Row Elements

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ABSTRACT: A statistical evaluation of ground state properties for first-row and second-row elements is presented. The present version MSINDO is compared with the previous version SINDO1 and other standard semiempirical methods. Significant improvements are achieved for heats of formation, bond lengths, bond angles, and ionization energies by MSINDO, which is now again competitive with other semiempirical methods. An extrapolation to bulk properties is given for ionic clusters of NaCl and MgO to demonstrate the transferability of the parameterization to large systems. Improvements for the electronic structure of compounds containing second-row elements are demonstrated with the MO diagram of an NaCl cluster with an F-center defect. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 572–578, 1999

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Introduction

In the preceding paper¹ we described the modification MSINDO of the SINDO1 formalism, including a new parameterization for the elements H, C, N, O, and F, and for Na to Cl. Here, we present a statistical evaluation of MSINDO results for compounds containing these elements with respect to heats of formation, structure data, ioniza-

tion energies, and dipole moments. Our results are compared with the previous SINDO1 version^{2,3} and other well-known semiempirical methods like MNDO,⁴ AM1,⁵ PM3,⁶ and MNDO/d.⁷ Second-row elements are compared with MNDO/d, because this method includes *d* orbitals for Al to Cl as MSINDO and SINDO1 do. This is known to be important for the description of hypervalent compounds. Furthermore, we want to show the transferability of the parameterization to larger systems with several hundreds of atoms. In the past a special parameterization was necessary for large clusters. An example is given for the extrapolation

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of NaCl and MgO cluster properties toward the bulk, which is compared with experimental data. Information about these clusters was included in the parameterization by small units up to trimers. Improvements are achieved by the new orthogonalization corrections¹ for compounds with second-row elements. This is demonstrated by an MO-level diagram of an NaCl cluster with an internal F-center defect.

Statistical Evaluations

The set of reference properties and molecules for first-row elements chosen was mainly from earlier parameterizations of SINDO1,^{8,9} but experimental reference values were updated and taken from refs. 10 and 11, except for ionization energies, which were taken from ref. 12. For second-row elements we used experimental data provided by Thiel in MNDO/d studies.^{13–15} It is noted that our set of properties was smaller than for the other semiempirical methods, due to the time-consuming explicit inclusion of zero-point energies for the calculation of heats of formation. For each molecule at a given parameter point, a complete Hessian of the energy with respect to all geometrical variables must be evaluated. Thus, we included as many molecules in the parameterization set as necessary to cover the different bonding situations of the elements. Therefore, a comparison with other semiempirical methods is of qualitative nature. Nevertheless, the set of molecules was large enough to show that MSINDO is competitive for all properties investigated.

We present a statistical evaluation of heats of formation, structure data, ionization energies, and

dipole moments. The results were obtained from single-determinant calculations without configuration interaction. For open-shell systems, the restricted Hartree–Fock (ROHF) scheme was used. Ionization energies were the first vertical values calculated via Koopmans's theorem. The dipole moments were calculated with the ZDO assumption.¹⁶ This approach was superior to the alternative backtransformation of the orthogonal density into the nonorthogonal basis with the inclusion of two-center dipole integrals. The same computer program and inputs were used for both the old SINDO1 and the new MSINDO version to avoid technical problems. Originally, first-row elements were adjusted to binding energies and second-row elements to heats of formation at 0 K in the previous SINDO1 version, but in this investigation they were treated with the same assumptions as presented in part I of this study.¹ The set of reference compounds and the corresponding experimental data changed in some cases, especially for second-row elements; therefore, the results for the previous SINDO1 version were somewhat different compared with earlier publications.^{8,9,17–21} Detailed information about the properties of all compounds included in the statistics of the following tables can be found elsewhere.²²

Table I lists the results for ground state properties of compounds containing first-row elements. If we compare both SINDO versions, the mean absolute error is reduced for all investigated properties in the present version. Considerable error reduction was achieved for heats of formation, bond lengths, and ionization energies. The error was reduced to about one half for the elements H, C, N, O. Improvements for fluorine compounds were less pronounced than for the group H, C, N, O,

TABLE I.
Mean Absolute Errors for Ground State Properties of First-Row Elements with Number of Values in Parentheses.

	Group	MSINDO	SINDO1	MNDO	AM1	PM3
ΔH_f (kcal/mol)	HCNO	5.12 (64)	9.49 (64)	6.26 (133)	5.52 (133)	4.23 (133)
	F	5.59 (25)	7.15 (25)	10.51 (43)	6.76 (43)	6.45 (43)
R (Å)	HCNO	0.011 (164)	0.019 (164)	0.015 (228)	0.017 (228)	0.011 (228)
	F	0.022 (46)	0.036 (46)	0.037 (124)	0.027 (124)	0.022 (124)
θ (°)	HCNO	1.84 (72)	2.56 (72)	2.69 (92)	2.01 (92)	2.22 (92)
	F	1.20 (22)	1.89 (22)	3.04 (68)	3.11 (68)	2.72 (68)
I (eV)	HCNO	0.44 (67)	0.84 (67)	0.47 (51)	0.36 (51)	0.43 (51)
	F	0.37 (16)	0.52 (16)	0.34 (40)	0.54 (40)	0.40 (40)
μ (D)	HCNO	0.34 (32)	0.49 (32)	0.32 (57)	0.25 (57)	0.27 (57)
	F	0.33 (17)	0.38 (17)	0.38 (40)	0.31 (40)	0.29 (40)

except for bond lengths. In comparison to other semiempirical methods the new version MSINDO reaches the same accuracy as PM3, which is known to give the best results among the standard methods. PM3 is better for heats of formation within the group H, C, N, O, but MSINDO is more accurate for fluorine. MSINDO yields the best results for bond angles and is close to PM3 for ionization energies. Dipole moments are better in AM1 and PM3. MNDO is less accurate than MSINDO for heats of formation and structure data. Bearing in mind the different number of reference properties investigated for first-row elements we conclude in saying that MSINDO has now the same high quality of results as the other well-known semiempirical methods, and provides a much more powerful tool for the prediction of ground state properties than before.

For second-row elements our aim was to include additional information on special compounds, which are the subject of our present investigations—that is, ionic crystals of NaCl and MgO, silicon clusters, and chlorosiloxanes. The main problem in all these cases was a rather poor description of large systems with the parameterization developed for small systems. In some cases (e.g., NaCl and MgO clusters), a different parameterization was necessary to reproduce lattice constants and binding energies observed in the bulk. Unfortunately, experimental gas phase data are rare for small units of these systems. The reference data we used were taken from high-level *ab initio*

calculations, namely Pople's G2²³ or G2(MP2)²⁴ methods, which are known to yield accurate results for atomization energies of first- and second-row elements, but are quite computer time consuming even for small systems. The largest systems of this kind, which we included in our parameterization, were (NaCl)₃, (MgO)₃ and Si₅. Experimental and *ab initio* data for silicon oxide compounds were provided by Thiel.¹⁴ We also added experimental structure data for Si₂OCl₆ and similar systems.²⁵ Mean absolute errors for ground state properties of all second-row elements are listed in Tables II to VI. The error for heats of formation of the old SINDO1 version was larger than expected, based on earlier work.^{17–21} The reason was the different set of reference molecules, in particular the inclusion of more hypervalent compounds and ionic systems. The large error for sodium and magnesium was mainly due to (NaF)₂, (NaCl)₂, (NaCl)₃, and (MgO)₃. Energies for the monomers have been well described with the earlier version, but the increase of the binding energy with unit size was too steep. Additionally, for magnesium, too few experimental data were available for carbon- and nitrogen-containing compounds. In other cases, the experimental reference values were updated by more recent values;¹³ for example, P₄O₆, where the change is about 150 kcal/mol. Usually, other properties were found to be in the expected range.

The most important improvements achieved by the new MSINDO version are in heats of forma-

TABLE II.
Mean Absolute Errors for Heats of Formation (kcal / mol) of Second-Row Elements with Number of Values in Parentheses.

Element	MSINDO	SINDO1 ^a	SINDO1 ^b	MNDO / d
Na	8.37 (13) 7.82 ^c (10)	4.7 (10)	37.58 (13) 6.71 (10) ^c	7.57 (23)
Mg	5.80 (25)	6.3 (12)	48.51 (25) ^d	9.61 (46)
Al	6.76 (16)	14.7 (21)	23.03 (16)	4.93 (29)
Si	6.69 (41)	9.2 (26)	14.37 (41)	6.33 (84)
P	4.83 (21) 3.89 (16) ^e	12.9 (23) 8.5 (17) ^e	29.14 (21) 18.86 (16) ^e	7.62 (43)
S	7.49 (24) 6.10 (14) ^e	10.8 (35) 7.9 (23) ^e	12.86 (24) 9.42 (14) ^e	5.57 (99)
Cl	7.13 (37) 6.42 (28) ^e	12.0 (36) 7.4 (33) ^e	33.66 (37) 10.55 (28) ^e	3.76 (178)

^aOld parameterization for compounds taken from previous work.^{17–21}

^bOld parameterization using the same assumptions for heats of formation and the same compounds as for MSINDO.

^cWithout ionic crystal clusters.

^dThe large error for magnesium is due to the lack of experimental data for carbon- and nitrogen-containing compounds in SINDO1.

^eWithout hypervalent compounds.

TABLE III.
Mean Absolute Errors for Bond Lengths (Å) of
Second-Row Elements with Number of Values
in Parentheses.

Element	MSINDO	SINDO1	MNDO / d
Na	0.051 (12)	0.079 (12)	0.120 (16)
Mg	0.030 (32)	0.103 (32)	0.120 (55)
Al	0.031 (13)	0.035 (13)	0.067 (20)
Si	0.018 (57)	0.055 (57)	0.047 (68)
P	0.019 (37)	0.031 (37)	0.048 (58)
S	0.022 (37)	0.028 (37)	0.040 (77)
Cl	0.037 (45)	0.044 (45)	0.038 (117)

tion. For all second-row elements the error is clearly less than 10 kcal/mol. The accuracy is comparable to MNDO/d, which yields excellent results for chlorine, but is not as good for magnesium. Bond lengths are improved for all second-row elements compared with previous SINDO1 version, with major improvements for sodium, magnesium, and silicon. MSINDO here has similar accuracies as MNDO/d for chlorine, and it is better for all other second-row elements. Bond angles are improved for sodium, aluminum, silicon and chlorine. Magnesium and phosphorus compounds are slightly less accurate than in the previous SINDO1 version. MNDO/d is better for magnesium, silicon, and chlorine, but in all other cases MSINDO gives better bond angles. Ionization potentials are improved for all second-row elements by the new version MSINDO, except for sodium, magnesium, and phosphorus, which are similar to the former version. MNDO/d is comparable for chlorine and phosphorus, but less accurate for the other elements. Dipole moments are better described by MNDO/d, except for sulfur and chlorine, for which MSINDO gives similar results. As expected, the

TABLE IV.
Mean Absolute Errors for Bond Angles (°) of
Second-Row Elements with Number of Values
in Parentheses.

Element	MSINDO	SINDO1	MNDO / d
Na	3.72 (5)	14.92 (5)	5.85 (4)
Mg	1.24 (10)	0.79 (10)	0.26 (18)
Al	2.87 (2)	4.01 (2)	4.45 (7)
Si	2.26 (37)	4.58 (37)	1.40 (41)
P	2.85 (19)	2.68 (19)	3.71 (37)
S	3.16 (28)	3.54 (28)	3.64 (55)
Cl	2.37 (32)	5.20 (32)	2.00 (79)

TABLE V.
Mean Absolute Errors for Vertical Ionization Energies
(eV) of Second-Row Elements with Number
of Values in Parentheses.

Element	MSINDO	SINDO1	MNDO / d
Na	0.32 (2)	0.33 (2)	—
Mg	0.23 (4)	0.26 (4)	0.35 (4)
Al	0.42 (9)	0.50 (9)	0.54 (8)
Si	0.40 (21)	0.62 (21)	0.54 (15)
P	0.70 (12)	0.66 (12)	0.68 (28)
S	0.48 (16)	0.72 (16)	0.57 (39)
Cl	0.32 (30)	0.39 (30)	0.33 (83)

overall error of all properties for second-row elements is slightly larger than for first-row elements, but the improved accuracy of the new version MSINDO is obvious. Our qualitative comparison has shown that the accuracy of MSINDO for second-row elements is now comparable to MNDO/d. This is noteworthy, because MSINDO avoids the dramatic increase of two-center, two-electron integrals in an *spd*-basis within the NDDO approximation. MSINDO realizes the achievements of the NDDO approximation in a much simpler way, by an improved treatment of the core Hamiltonian matrix. On the other hand, MNDO/d does not explicitly calculate zero-point energies and saves computer time in this way.

Special Systems

The major goal of our parameterization was to bridge the gap between properties of small molecules and very large systems with nearly bulk character. An area that demands exactly this wide range of flexibility is adsorption of small molecules

TABLE VI.
Mean Absolute Errors for Dipole Moments (D) of
Second-Row Elements with Number of Values
in Parentheses.

Element	MSINDO	SINDO1	MNDO / d
Na	0.72 (3)	0.55 (3)	0.31 (5)
Mg	0.72 (1)	1.15 (1)	—
Al	0.58 (1)	0.64 (1)	—
Si	0.55 (14)	0.68 (14)	0.42 (14)
P	0.69 (13)	1.01 (13)	0.33 (17)
S	0.40 (15)	0.43 (15)	0.42 (25)
Cl	0.26 (12)	0.43 (12)	0.30 (62)

at ionic crystal surfaces. If we intend to examine the adsorption of water at MgO clusters, the parameters must correctly describe the Mg-O bond within the crystal and the Mg-O bond to the molecular or dissociative adsorbed water molecule at the same time. In the past, this problem was circumvented by readjusting the bond parameters to bulk properties. A procedure that allows extrapolation of binding energies and lattice constants to the bulk was developed by Jug and Geudtner.²⁶ Our parameters provide a good description of the properties of small systems, as can be seen in Tables I to VI. We can demonstrate that no further adjustment of parameters is necessary for large systems. The inclusion of small units up to (NaCl)₃ and (MgO)₃ during parameterization was sufficient to cover the properties of these ionic crystals. Figures 1 and 2 show normalized binding energies and lattice constants, depending on the relative average coordination number, *k*, for NaCl clusters, as described previously.²⁶ *k* is defined in the following way. The coordination numbers of all atoms in the cluster are averaged and normalized to the bulk coordination value, which is 6 for NaCl and MgO bulk. Therefore *k* = 0.5 for the Na₄Cl₄ cube and *k* = 0.9 for the Na₅₀₀Cl₅₀₀ cube. Figures 3 and 4 show the results for MgO clusters. Experimental bulk values for heats of formation and lattice constants are indicated by dashed lines.

It is gratifying that the new version MSINDO reaches the same quality for *k* = 1 (bulk value) as the previous SINDO1 version, which used specially adjusted parameters. For both systems, NaCl and MgO, the binding energies for the bulk are

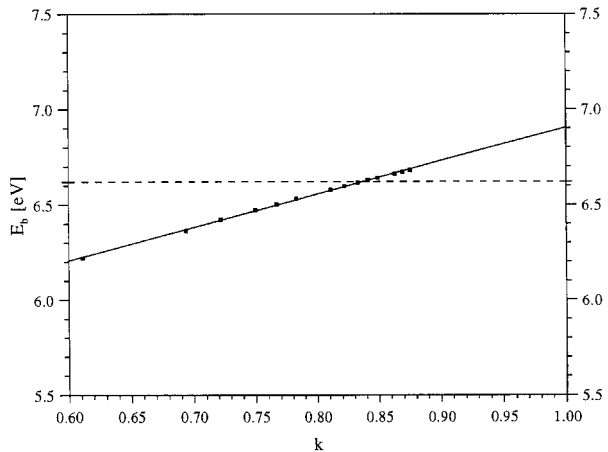


FIGURE 1. Binding energy per unit *E_b* (eV) in dependence of relative average coordination number *k* for NaCl.

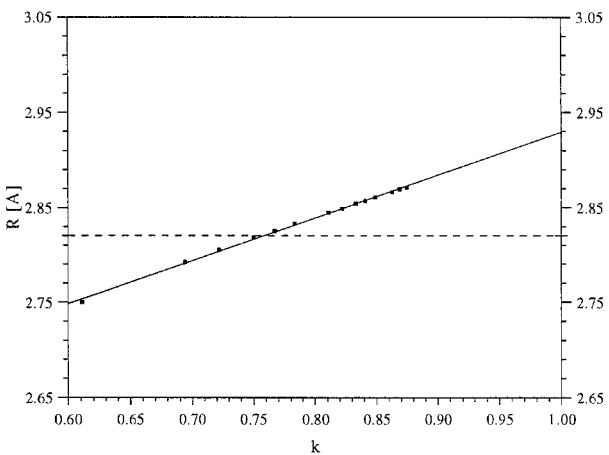


FIGURE 2. Lattice constant *R* (Å) in dependence of relative average coordination number *k* for NaCl.

slightly too high and the lattice constants are slightly too long, but relative deviations are small. If we take into consideration that binding energies have to be corrected by the inclusion of zero-point energies in our approach, the agreement for energies would be even better. But zero-point energies cannot be obtained in this procedure, because the clusters are not allowed to relax with respect to all degrees of freedom. The main advantage of the new MSINDO version is the correct behavior seen on both sides of Figures 1 to 4. This means that, for example, the Na-Cl bond is as correctly described in a single molecule as it is in very large clusters, which is an important condition if one intends to study the growth of NaCl molecules to NaCl clus-

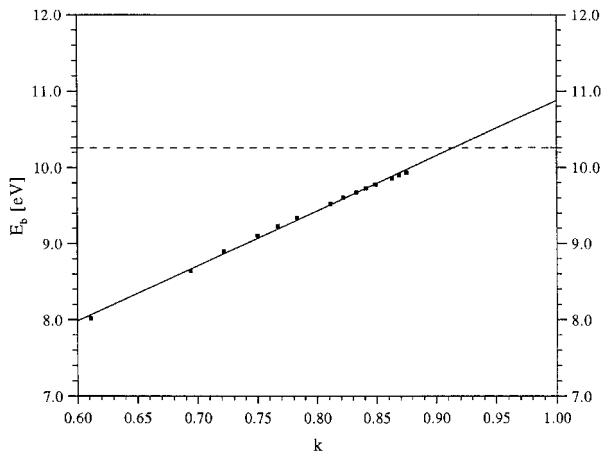


FIGURE 3. Binding energy per unit *E_b* (eV) in dependence of relative average coordination number *k* for MgO.

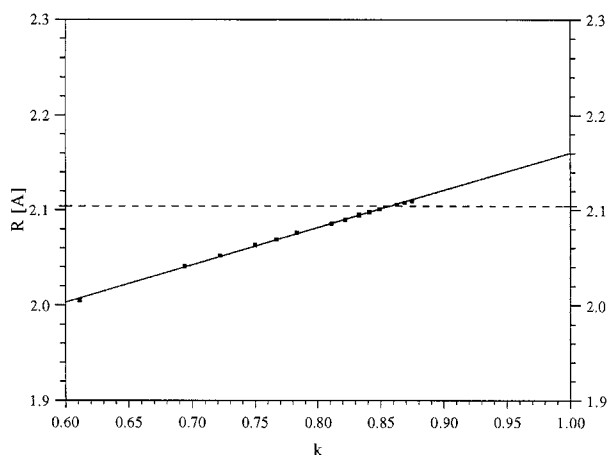


FIGURE 4. Lattice constant R (Å) in dependence of relative average coordination number k for MgO.

ters. This result justifies our approach of extending the reference set of molecules with small units of ionic crystals. It would be ideal to make this set of reference molecules as large as possible by including all possible bonding situations of the elements. However, in practice, the limit is set by the availability of reliable experimental data and by the speed of computers.

Another noteworthy improvement of the new version MSINDO has been achieved for the electronic structure of compounds containing second-row elements. As described in part 1 of this series, the old SINDO1 formalism of orthogonalization corrections led to improper relative bonding contributions of s and p orbitals,¹ which can be seen from Figure 5, where the MO diagram of an NaCl $5 \times 5 \times 4$ cluster with an internal chlorine defect (F center)²⁷ is plotted. Energy levels of virtual orbitals have been corrected by the IVO (improved virtual orbital) method.²⁸ Also, the energies of the partially filled orbitals have been corrected, as described by Sauer et al.²⁹ The conduction band was broadened and the defect state (circled) shifted toward the conduction band. The corresponding beta level was even shifted into the conduction band. Resulting excitation energies obtained from configuration interaction single excitations for the F center were about 1.4 eV smaller than the experimental value of 2.77 eV.²⁷ In Figure 6, the corresponding MO diagram calculated with the new MSINDO version is plotted.

The qualitative picture is much better now. The virtual levels are closer together and the defect state is located in the gap between the valence

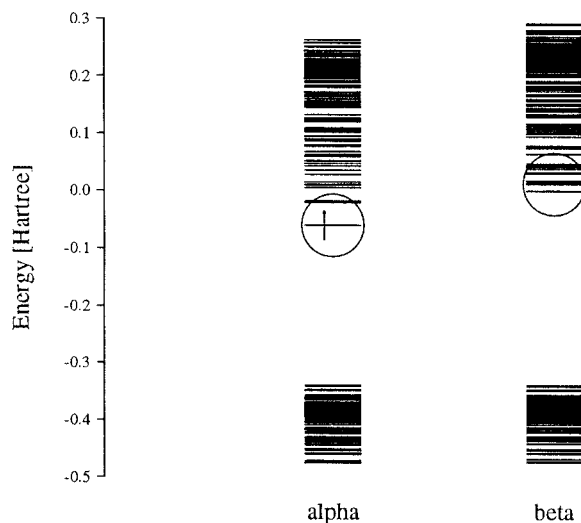


FIGURE 5. SINDO1 MO diagram of a $5 \times 5 \times 4$ NaCl cluster with bulk F center.

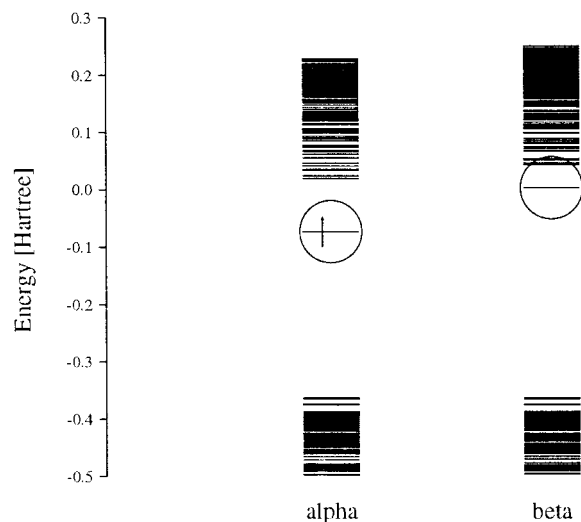


FIGURE 6. MSINDO MO diagram of a $5 \times 5 \times 4$ NaCl cluster with bulk F center.

band and conduction band. Excitation energies are now in the experimental range and are about 0.2 eV larger than the experimental value, as expected at the HF level. Detailed studies of defective NaCl and MgO clusters for excitation energies and adsorption of small molecules are in progress.

Conclusions

The consistent modification MSINDO of SINDO1 presents a major improvement over pre-

vious versions of the SINDO method for first- and second-row elements. Predictions for second-row elements are slightly less accurate than for first-row elements. The superiority of the new MSINDO version compared with the old one is apparent for all kinds of properties investigated, especially for heats of formation and bond lengths. MSINDO is now quite competitive compared with other standard semiempirical methods and has proven to be capable of reproducing properties of both small molecules and systems with bulk structure. Extension of the new MSINDO version to the remaining first-row elements and third-row transition metal elements is in progress.

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